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US 4299754 A

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(54) Aqueous coating composition

(57) An aqueous coating composition is characterized by dispersing a graft copolymerized α,β -unsaturated dicarboxylic acid or its acid anhydride grafted onto propylene- α -olefin copolymer, a neutralizing base and a polyol into water, and has excellent adhesion to polyolefin and good stability and can be converted to aqueous dispersion without use of an aromatic organic solvent.

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AQUEOUS COATING COMPOSITION.

5 The present invention relates to an aqueous coating composition suitable for application to primer and paint to be used in painting polyolefinic resin moldings and which contain no aromatic organic solvent.

10 Polyolefinic resins such as polypropylene have been used extensively for electrical appliances in the house, in motor cars, etc. because of their excellent properties and low price. However, polyolefinic resins have the drawback that they are difficult to paint and
15 adherence is poor due to non-polarity. For this reason, it is common to use a primer having a chlorinated polyolefin as a major ingredient at the time of painting and adhering polyolefinic resins. However, since chlorinated polyolefin only dissolves in
20 aromatic organic solvents such as toluene and xylene, large amounts of aromatic organic solvent are required, which has been a problem from aspects of safety and hygiene and also environmental pollution.

25 Hence, various attempts to produce aqueous dispersion of chlorinated polyolefin have been made and they are disclosed, for example, in Japanese Unexamined Patent Publication No. Hei 1-153778, No. Hei 1-256556 and Hei 2-284973. In these, however, aromatic organic
30 solvents are used in production and it was difficult to eliminate them completely. Also, attempts to produce aqueous dispersions of modified polyolefins have been made, which are disclosed, for example, in Japanese Unexamined Patent Publication No. Sho 59-47244

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and No. Hei 2-286724. They have however, drawbacks
such as poor adhesion to polyolefin resins, poor water
resistance and poor paintability and such aqueous
compositions have not yet been put into practice.

As described, it is necessary to employ a primer
treatment to perform the painting and adhesion to
polyolefinic resin, but the production of aqueous
compositions for paint containing no aromatic organic
solvent at all and having good adhesion to polyolefinic
resin has been difficult technically. The purpose of
the present invention is to provide an aqueous
composition which solves such problems and improves
paintability and adhesion of polyolefinic resin.

As a result of extensive studies to this end the
inventors have reached the present invention.

Thus, the invention provides an aqueous coating
composition for a polyolefinic resin comprising (a) a
resin graft copolymerized α, β -unsaturated dicarboxylic
acid or its acid anhydride onto a propylene- α -olefin
copolymer in an amount of 1 to 20% by weight, a
neutralizing base and (b) a polyol dispersed in water.

In the following, the invention will be
illustrated in detail.

The propylene- α -olefin copolymer of component (a)
in the aqueous coating composition of the invention is
a random copolymer or block copolymer of propylene with

5 α -olefin. The random copolymer is preferred. As α -
olefins, ethylene, butene-1, pentene-1, hexene-1, etc.
can be mentioned and two or more of these may be
copolymerized. Among these, ethylene or 1-butene is
preferable from the point of physical properties of the
resin. Moreover, the proportion of the propylene
10 component is preferably not less than 55 mol %. If
less than 55 mol %, then adhesion to polypropylene is
poor, which is, of course, undesirable.

15 For α, β -unsaturated dicarboxylic acids or their
acid anhydrides to be graft copolymerized onto
propylene- α -olefin copolymer, for example, maleic acid,
fumaric acid, itaconic acid, citraconic acid,
allylsuccinic acid, mesaconic acid and aconitic acid,
and their acid anhydrides can be listed as examples.
The amount for graft copolymerizing α, β -unsaturated
20 dicarboxylic acid or its acid anhydride is preferable
to be 1 to 20 % by weight. If under 1 % by weight,
the stability on dispersion in water will become poor
and, if over 20% by weight, the grafting efficiency
decreases, which is uneconomical. Two to ten % by
25 weight is particularly preferable.

30 Moreover, the weight average molecular weight of
resin graft copolymerized α, β -unsaturated dicarboxylic
acid or its acid anhydride is preferably 3000 to 35000.
If under 3000, the cohesion will be insufficient
resulting in poor adhesion to the polyolefinic resin
and, if over 35000, the manipulability on dispersing
into water will become poor, which is undesirable.
Bringing the molecular weight in this range is possible
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5 by selecting the molecular weight of the raw material
or the conditions at the time of conducting the
grafting reaction, and it can also be performed so
that, after once decreased the molecular weight of raw
10 material, grafting reaction is conducted. Besides, the
weight average molecular weight can be determined by
GPC (gel permeation chromatography).

15 Graft copolymerization of α, β -unsaturated
dicarboxylic acid or its acid anhydride onto propylene-
 α -olefin copolymer may be conducted by a known method,
but it is particularly preferable to use a method
wherein the propylene- α -olefin copolymer is molten
above its melting point under heat and the graft
20 copolymerization is conducted in the presence of a
radical-generating agent.

25 When using this method, a reactor equipped with
an intensive agitator, Banbury mixer, kneader, extruder
or the like is employed and α, β -unsaturated
dicarboxylic acid or its acid anhydride and a radical-
generating agent are added at a temperature of not
lower than about 150 °C to not higher than about 300 °C
to react, and the product is pelletized by known
method.

30 As an alternative method, it is also possible to
dissolve the propylene- α -olefin copolymer in an organic
solvent such as xylene under heat and conducted the
reaction in the presence of a radical-generating agent,

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5 but this method is less preferred because it is time-consuming to remove the organic solvent and there is sometimes residual organic solvent.

10 The radical-generating agent to be used for the reaction can be appropriately selected from known materials, but an organic peroxide is particularly preferable. As the organic peroxides, for example, benzoyl peroxide, dicumyl peroxide, lauroyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane-3, di-t-butyl
15 peroxide, t-butyl hydroperoxide, t-butyl peroxybenzoate and cumene hydroperoxide, can be mentioned, which are selected for use depending on the reaction temperature.

20 For the polyols of component (b), a wide range of materials such as diol, polyoxyalkyldiol, hydroxy-terminated polybutadiene, polyvalent alcohols such as glycerine, polyesterpolyol, acrylicpolyol, polyurethanepolyol and bisphenol A can be used. For example, ethylene glycol, diethylene glycol,
25 triethylene glycol, propylene glycol, dipropylene glycol, butanediol, pentanediol, hexanediol, glycerine, etc. can be mentioned. Thereamong, polyols with strong hydrophilicity are desired.

30 The molecular weight of the polyol is preferably not more than 1000. If over 1000, the stability of composition dispersed in water will become poor, which is unpreferable.

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5 This polyol is preferable to be used in a
proportion of 4 to 200 parts by weight per 100 parts by
weight of component (a). If under 4 parts by weight,
then it is difficult to perform the dispersion in water
and the flexibility of the paint film decreased, which
is undesirable depending on the application. If over
10 200 parts by weight, then the water resistance of the
film foamed with such a composition is in danger of
becoming poor.

15 The reason why component (a) is neutralized with
base is for ionizing carboxyl group, thereby achieving
a good dispersion into water. Suitable basis include
sodium hydroxide, potassium hydroxide, ammonia,
methylemine, ethylemine, propylamine, butylamine,
hexamine, octylamine, ethanolamine, propanolamine,
20 diethanolamine, N-methyldiethanolamine, dimethylamine,
diethylamine, triethylamine, N,N-dimethylethanolamine,
2-dimethylamino-2-methyl-1-propanol, 2-amino-2-methyl-
1-propanol and morpholine.

25 Since the degree of hydrophilicity of the resin
differs depending on the types of base to be used, it
is necessary to select appropriately depending on the
conditions, but amines having a hydroxyl group such as
ethanolamine and 2-amino-2-methyl-1-propanol are
30 preferable due to their strong hydrophilicity. The
amount of base used is suitably in a range of 0.3 to
1.5 times as much as the equivalent weight to carboxyl
group of component (a) and 0.5 to 1.2 times are
preferable.

5 Dispersing components (a) and (b) into water can
be performed by a method wherein component (a) is
allowed to melt by heating it to a temperature above
its melting point, component (b) and the base and, if
need be, a surfactant are added, and water is added to
10 the mixture of these with agitation. According to
another embodiment of the method, the mixture of these
is added to water or all the components including water
are mixed and agitated under heat. Moreover, if
performing at high temperature and under pressure, a
15 dispersion with good stability can be obtained.

Dispersing is possible either with or without
using a surfactant, but it is desirable to use a
surfactant when the amount of α, β -unsaturated
20 dicarboxylic acid or its acid anhydride having been
graft copolymerized is low. The use level is
preferable to be not more than 25 % to component (a).
If over 25 %, the water resistance of paint film will
become poor.

25 Any type of surfactant can be used, but nonionic
surfactants are desirable because of their low
toxicity, and, using this mainly, anionic surfactant or
fluorosurfactant may be used in combination.

30 As the nonionic surfactants, polyoxyethylene
alkyl ester, polyoxyethylene alkyl ether,
polyoxyethylene alkylphenyl ether, sorbitan alkyl
ester, polyglycerine ester, etc. can be exemplified.

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As the anionic surfactants, carboxylate, sulfonate, salt of sulfate, salt of phosphate, etc. are mentioned. For the fluorosurfactants, all of anionic, nonionic and cationic types can be used. In addition to these, pluronic type can also be used as a high molecular surfactant.

The inventive composition dispersed into water in this way has excellent adhesion to polyolefin, in particular, polypropylene and is excellent as a primer on painting and adhesion. Also, the stability is good. Further, the flexibility appears in the paint film, which is preferable. The aqueous coating composition of the invention may be blended with pigments as it is and may be blended with other aqueous resin components. It can be painted onto the substrate resin by roll coating, spraying and brush coating, etc. It is also possible to use as an top coating paint by adding other components.

The aqueous coating composition of the invention contains propylene- α -olefin copolymer graft copolymerized with α,β -unsaturated dicarboxylic acid or its acid anhydride as one of components, hence it is excellent in adhesion to polyolefin. Moreover, it has polyol as a component, and, by neutralizing this with a base, it was found possible to convert to an aqueous dispersion, which has been difficult hitherto, providing also good stability.

The invention is further illustrated by the following Examples.

Production example 1

In a four-neck flask fitted with agitator, cooling tube and dropping funnel, 300 g of propylene-butene-ethylene copolymer (propylene component 68 mol %, butene component 24 mol % and ethylene component 8 mol %, weight average molecular weight 68000) was molten under heat. Then, keeping the temperature of system at 180 °C, 25 g of maleic anhydride and 5 g of dicumyl peroxide were added dropwise each over 3 hours while agitating, and thereafter reaction was conducted for 3 hours. After the reaction, the reaction product was cooled to room temperature, and then it was thrown into large amounts of acetone for purification to obtain a graft copolymer with grafting amount of 4.8 %. When measuring the molecular weight by GPC, it showed a weight average molecular weight of 26000.

For the measurement of weight average molecular weight, column TSK-GEL was attached to HLC-8020 made by Tosoh Corp. and the sample was dissolved into THF (tetrahydrofuran) to measure at 40 °C. The molecular weight was determined from a calibration curve formed with polystyrene standard samples.

Production example 2

By similar manipulation to Production example 1, 40 g of maleic anhydride and 8 g of di-t-butyl peroxide were reacted 300 g of propylene-ethylene copolymer (propylene component 75 mol %, weight average molecular weight 85000) to obtain a graft copolymer with grafting amount of 9.2 %. The weight average molecular weight was 22000.

Production example 3

By similar manipulation to Production example 1, maleic anhydride was graft reacted with propylene-ethylene copolymer (propylene component 50 mol %, weight average molecular weight 180000) to obtain a graft copolymer with grafting amount of 6.2 %. The weight average molecular weight was 75000.

Example 1

In a flask equipped with agitator, 150 g of ethylene glycol and 25 g of surfactant (Nonion NS-212, made by Nippon Oil and Fats Co.) were placed, mixed and heated to 100 °C, and 100 g of graft copolymer of Production example 1 were added little by little while agitating intensively. After the graft copolymer melted, 4 g of ethanolamine were added. Keeping the temperature at 100 °C, water of 90 °C was added little by little while agitating intensively. At the point of having added 300 g of water, contents were taken out. The contents showed a milky white liquor.

Examples 2 through 5

Performing similar manipulation to Example 1, resins of production examples were dispersed into water with formulation compositions shown in Table 1.

Comparative examples 1 and 2

By similar manipulation to example, resins were dispersed into water with formulation compositions shown in Table 1.

Table 1

[Figures indicate parts by weight]

	Graft copolymer		Polyol		Surfactant		Base	
Example 1	Production example 1	100	Ethylene glycol	150	NS-212	25	Ethanolamine	4
Example 2	Production example 1	100	Butanediol	8	NS-212	25	Ethanolamine	4
Example 3	Production example 1	100	Polyethylene glycol 400	180	NS-212	25	Ethanolamine	6
Example 4	Production example 2	100	Propylene glycol	50	NS-212	25	Triethylamine	5
Example 5	Production example 2	100	Tetraethylene glycol	200	NS-212	10	Morpholine	6
Comparative example 1	Production example 1	100	None	0	NS-212	25	Ethanolamine	4
Comparative example 2	Production example 3	100	Ethylene glycol	150	NS-212	25	Ethanolamine	4

The stability of aqueous dispersions of Examples 1 through 5 and Comparative examples 1 and 2 after allowed to stand for 1 month are shown in Table 2.

Examples 6 through 10

Each of aqueous dispersions of Examples 1 through 5 were coated onto a polypropylene resin plate by spraying and dried for 30 minutes at 80 °C. Next, two-component urethane upper coating paint was painted and, after allowed to stand for 10 minutes at room temperature, it was dried forcedly for 30 minutes at 80 °C using fan dryer. After the painted plate thus obtained was allowed to stand for a day at room temperature, tests of paint film were made. Results are shown in Table 2.

Comparative examples 3 and 4

Tests were made similarly to Examples 6 through 10. Results are shown in Table 2. Besides, in the case of

Comparative example 3, the spray coating was impossible.

Table 2

	Composition	Stability	Adhesive property	Gasoline resistance
Example 6	Example 1	Good	100/100	Good
Example 7	Example 2	Good	100/100	Good
Example 8	Example 3	Good	100/100	Good
Example 9	Example 4	Good	100/100	Good
Example 10	Example 5	Good	100/100	Good
Comparative example 3	Comparative example 1	Separation	—	—
Comparative example 4	Comparative example 2	Good	60/100	Peeling-off

Besides, the test methods are as follows:

• Adhesive property

Nicks reaching the base were made on the surface of paint film with cutter to form a hundred cross-cuts at intervals of 1 mm. By closely contacting cellophane adhesive tape there-with and by peeling off in the direction of 180°, the number of remaining cross-cuts was counted.

• Gasoline resistance

Nicks reaching the base were made on the surface of paint film and, after immersed into regular gasoline for 4 hours, the state of paint film was observed visually.

The aqueous coating composition of the invention is excellent in the adhesive property to polyolefin and has good stability and good flexibility of paint film. Yet, conversion to aqueous dispersion is possible without using aromatic organic solvent at all, hence the invention is excellent in the aspects of safety and hygiene and environmental pollution.

CLAIMS:

1. An aqueous coating composition for a polyolefinic resin comprising a graft copolymerized resin of α,β -unsaturated dicarboxylic acid or its acid anhydride and propylene- α -olefin copolymer in an amount of 1 to 20% by weight, a neutralizing base and a polyol dispersed in water.
2. An aqueous coating composition according to claim 1, wherein the propylene component of the propylene- α -olefin copolymer is not less than 55 mol %.
3. An aqueous coating composition according to Claim 1 or 2, wherein the weight average molecular weight of the graft copolymerized resin is 3000 to 35000.
4. An aqueous coating composition according to any of claims 1 to 3, wherein the molecular weight of the polyol is not more than 1000.
5. An aqueous coating composition according to any of claims 1 to 4, wherein the amount of polyol is 4 to 200 parts by weight per 100 parts by weight of graft copolymerized resin.
6. A method of preparing aqueous coating composition for a polyolefinic resin comprising the steps of neutralizing a graft copolymerized resin of α,β -unsaturated dicarboxylic acid or its acid anhydride and propylene- α -olefin in an amount of 1 to 20 % by weight and a polyol with a base and dispersing the components in water.

- 14 -

Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

Application number

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Relevant Technical fields

(i) UK CI (Edition L) C3V: VABA, VABM, VABP, VABR,
VABS, VEA

(ii) Int CI (Edition 5) C09D

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI

Search Examiner

M J PRICE

Date of Search

29 JUNE 1993

Documents considered relevant following a search in respect of claims 1-6

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
A	EP 0396055 (NISSAN)	1
A	US 4946895 (SUMITOMO)	1
A	US 4299754 (MITSUI)	1

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

PATENT ABSTRACTS OF JAPAN

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(54) PRIMER COMPOSITION AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To obtain a primer composition desirable as, e.g. a coating material component or a primer, which can give a coating film having good film properties when applied to a substrate, has a suitable solution viscosity, does not undergo stringing and sadding in the coating work, and therefore has an excellent workability in coating.

CONSTITUTION: This composition comprises (A) a chlorinated modified polyolefin resin which contains 0.1-10wt.% graft comonomer units comprising at least one member selected between an unsaturated carboxylic acid and its anhydride and grafted onto a polyolefin, in which at least a part of the carboxyl groups of the graft copolymer units are bonded to an epoxy compound, and which has a chlorine content of 5-35wt.% and (B) an organic solvent.

LEGAL STATUS

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